

Ignition Characteristics of Colorado Oil Shale

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Introduction

Spontaneous ignition is usually characterized by an abrupt (exponential) increase in temperature and results when the rate of heat production in exothermic reaction exceeds the rate of heat dissipation to the surrounding media. Ordinarily the term spontaneous ignition temperature is applied to those systems being oxidized by air. However, in this paper the term applies to systems using oxygen enriched or partially depleted gas streams.

In a practical application it is important to know the ignition characteristics of oil shale in developing an understanding of processes for recovering oil from oil shales. This is particularly true when using the countercurrent or reverse combustion in situ recovery or the parallel flow retorting process (1, 2).

The countercurrent combustion process is one in which the combustion or oxidation zone moves against the flow of the injected gas stream. Figure 1 shows a schematic representation of such a process. To be practical, the combustion zone must progressively move toward the source of the oxidant injection at such a rate that only a minimum amount of fuel is consumed and the useful products produced in an oxygen free atmosphere. The process is somewhat unconventional but has been demonstrated in the laboratory as a means of producing oil from oil shale.

One way of explaining why the process works is as follows: As ignition of a given particle takes place, it is accompanied by an exponential temperature rise which in turn causes a rapid increase in combustion (oxidation) rate. This effectively removes the oxygen from the surrounding gas stream, so no further oxidation takes place at this point. However, heat has been transferred to the surrounding particles as well as the gas stream. One effect is that particles immediately upstream are continuously being heated to their ignition temperature and the process repeats itself with the combustion zone effectively progressing against the gas flow. Another effect is that the oxygen has been efficiently removed from the gas downstream from the combustion zone. This provides an inert hot gas in which the hydrocarbon components are effectively distilled from the solids.

Experimental

In this investigation the ignition temperatures were determined in a flow-type system so that conditions would be somewhat comparable to the retorting process. The experimental arrangement is given in Figure 2.

The basic unit of equipment was a small Inconel block furnace containing two one-half inch sample holes. One hole contained the sample and the other was filled with an inert reference material. Alternate junctions of twelve chromel-alumel thermocouples were located in the two holes to form a sensitive thermopile detector.

Since ignition is characterized by a rapid temperature rise, the differential thermopile was used in most experiments to detect the temperature at which combustion

occurred. However, advantage was also taken of the fact that ignition is also accompanied by the simultaneous release of carbon dioxide. In the latter case, the gas stream was continually monitored as a function of temperature with a differential thermal conductivity cell. Both techniques proved equally effective.

Determinations were made in air and in gas mixtures of oxygen and nitrogen over a pressure range from atmospheric to 1000 psig. The gas mixtures contained six, thirteen, twenty-one, and fifty-five percent by volume of oxygen.

In a typical experiment, about two grams of -40 to 60 mesh oil shale was placed in the sample hole. A similar sized sample of previously pyrolyzed oil shale was placed in the reference cell. The oxidant containing gas passed at the same rate through the shale and the reference material at the pressure of the experiment. The block was heated at a uniform rate of about 40°F/minute. Temperature and differential temperature were recorded by use of either a two-pen or an x-y recorder. In the alternate detection system the off-gas was taken from the cells, passed through drying tubes to remove water vapor, and then to the reference and sample sides, respectively, of a thermal conductivity detector. This signal was then continuously recorded as a function of the sample temperature.

Experimental Results

Ignition temperatures as a function of oxygen partial pressure for data covering several oxygen concentrations in the gas stream are tabulated in Table I and shown in Figure 3. (Note: These data are plotted with the square root of the oxygen partial pressure as a coordinate so that the scale could be expanded on the low pressure end and still extrapolated to zero. Plotting the square root has no other significance). From the curve shown in Figure 3 it is readily observed that the ignition temperature is relatively independent of total pressure, but strongly dependent on the oxygen concentration.

Other data have shown that lower rates of supplying the oxygen has little or no effect on the ignition temperature as long as excess oxygen is present for the combustion reaction.

One interesting set of data are shown in Figure 4. Of particular interest are the characteristics of the ignition temperatures at pressures below 100 psig where two temperature peaks were noted. The first peak showed a temperature rise but did not result in ignition.

These same data are plotted as a function of oxygen partial pressure in Figure 5, which shows the nature of the transition region clearly. It is thought that this transition region is associated with the well known "cool flame" oxidation phenomena observed for ignition of many hydrocarbons as a function of pressure. For example, Figure 6 shows these oil shale data, together with ignition curves, for n-octane, i-octane, and propane (3, 4). Naturally one would not expect the data to coincide with these particular hydrocarbons, but the similarity of the shape of the curves and the temperature range is striking. One possible interpretation of this behavior is that the shale ignition is associated with gas phase combustion of hydrocarbons being distilled out of the oil shale.

Discussion

The question arises why oil shales ignite at such low temperatures when destructive distillation of the shale oil does not occur until temperatures in excess of 700°F are reached.

This question can possibly be answered by considering the fact that Colorado oil shale has from one to three percent by weight (about ten percent of total

TABLE I

<u>Gas Composition</u> <u>Volume %</u>	<u>Total Pressure</u> <u>(psi)</u>	<u>*Oxygen Partial</u> <u>Pressure (psi)</u>	<u>Ignition</u> <u>Temperature (°F)</u>
(Air)	125	24	450
(21% O ₂)	162	34	435
	212	44	435
	587	123	385
	954	203	365
	22.2	4.7	545
	32.2	6.8	540
	32.2	6.8	535
	52.2	11.0	500
	72.2	15.1	475
	26.2	5.5	530
	92.2	19.4	465
	112.0	23.6	455
	212.0	44.5	425
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(55% O ₂)	22.2	12.2	455
(45% N ₂)	112	61.7	400
	210	116	375
	512	281	354
	812	446	340
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(13% O ₂)	22.2	2.9	580
(87% N ₂)	44.2	5.7	560
	60.2	7.8	500
	110	14.4	495
	167	21.8	453
	594	77.3	395
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(6% O ₂)	22.2	1.3	586
(94% N ₂)	39.2	2.4	565
	62.2	3.7	535
	112	6.7	506
	277	16.6	435
	860	51.6	405

*Data taken at gas flow rate of 1350 standard cubic feet per square foot of cross sectional area per hour.

organic matter) of benzene soluble components in it. As shown in Figure 7, about the same weight fraction of oil shale is volatile between 360°F and 700°F when analyzed by thermogravimetric (TGA) techniques. These data indicate that volatiles start being evolved in an appreciable amount at about 360°F, which was about the same as the lowest self ignition temperature observed. Further, this preliminary evolution reaches a maximum at about 600°F, which is about the normal ignition temperature in air at atmospheric pressure.

Based on these data, it seems very likely that ignition is associated with the evolution of hydrocarbon vapors from the oil shale in the temperature range 360°-700°F.

Summary

The self ignition temperature of Colorado oil shale has been determined to vary with oxygen concentration from about 630°F at atmospheric conditions to 360°F at high (about 500 psi) oxygen partial pressure.

The ignition temperature is shown to correspond closely to temperature range during which organic vapors evolve prior to the onset of destructive distillation of the kerogen in the shale.

Literature Cited

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4. Maccormac, M., and Townsend, D. T. A., The Spontaneous Ignition Under Pressure of Typical Knocking and No-Knocking Fuels: Heptane, Octane, Iso-octane, etc. J. Chem. Soc. 143 (1940).

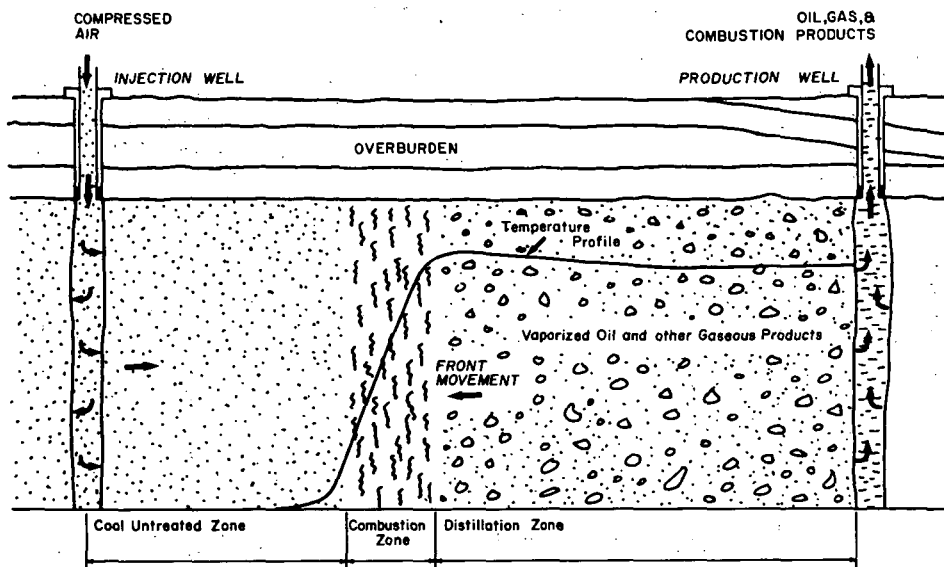


Figure 1. The Countercurrent Combustion In Situ Process for Recovering Hydrocarbons.

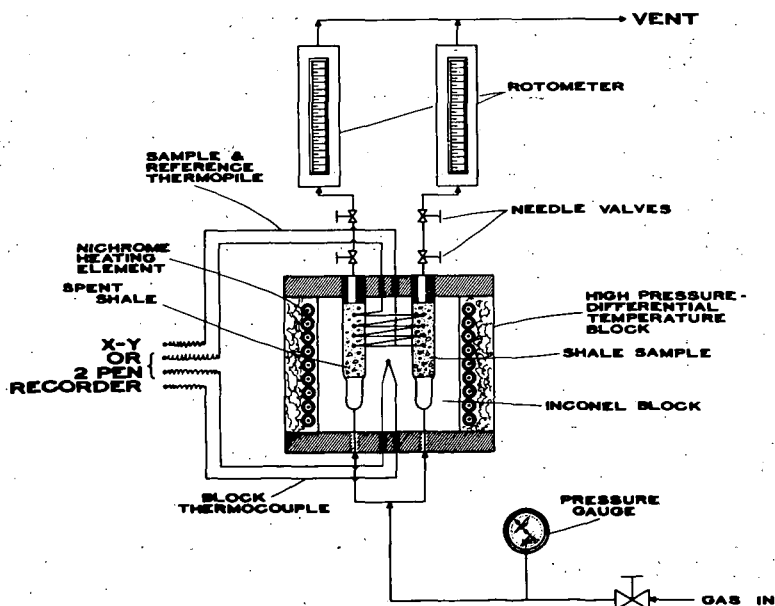


Figure 2. High Pressure Differential Analysis Equipment for Determining Spontaneous Ignition Temperature of Oil Shale.

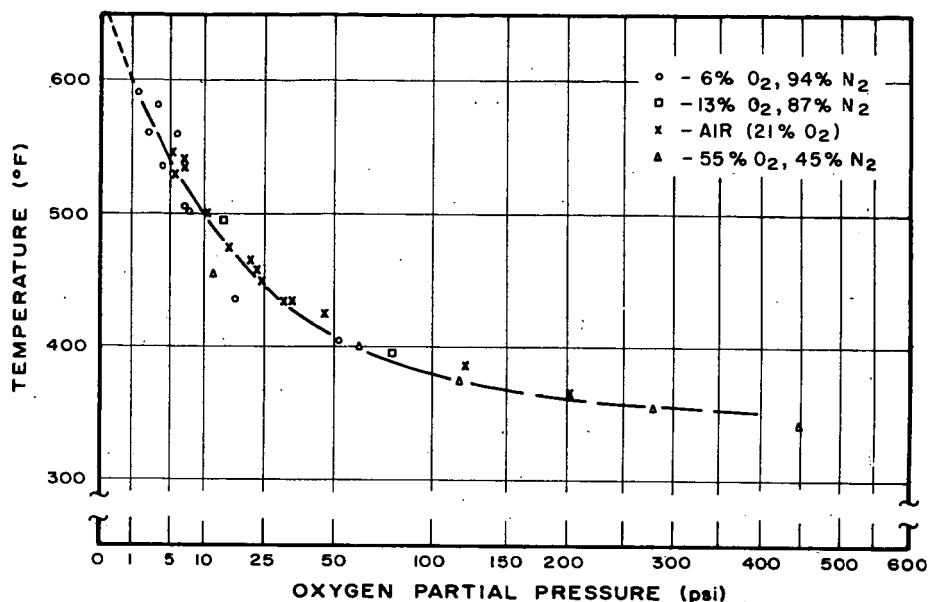


Figure 3. Ignition Temperature of Colorado Oil Shale as a Function of Oxygen Partial Pressure.

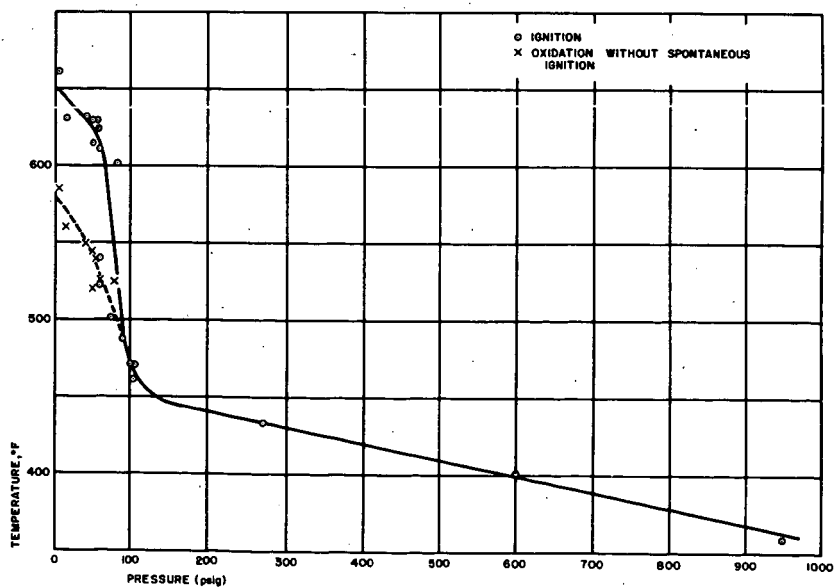


Figure 4. Spontaneous Ignition Temperature of Colorado Oil Shale as a Function of Pressure.

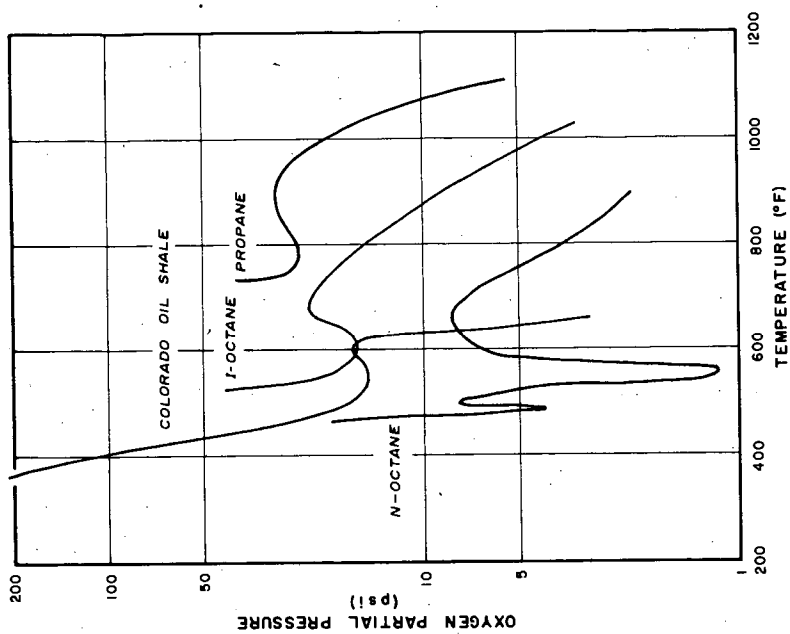


Figure 6. Spontaneous Ignition Curves for Selected Hydrocarbons.

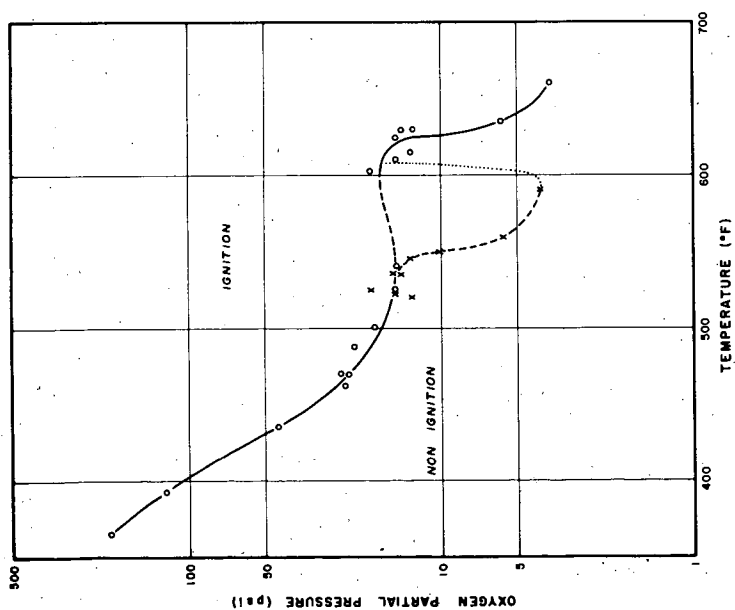


Figure 5. Spontaneous Ignition Curve for Colorado Oil Shale.

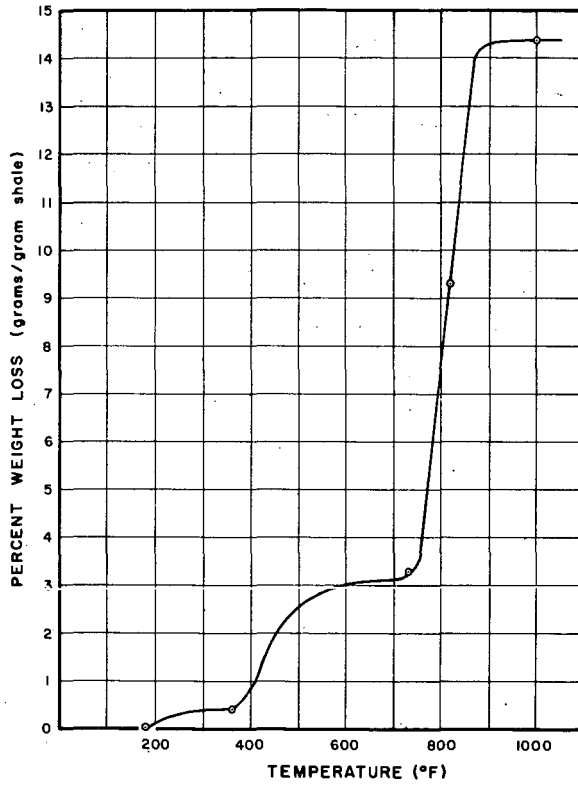


Figure 7. TGA of Colorado Oil Shale.